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14. ABSTRACT
This work presents the results of an investigation into the structure/property relationships of a series of cyanate ester resins prepared from a renewable precursor derived from lignin. These materials possess favorable thermal and water uptake properties with dry glass transition temperatures above 200°C and wet glass transition temperatures above 175°C with water uptake below 4%. Char yields of the resins were around 30% under nitrogen and around 10% in air. Differential scanning calorimetry showed that resins with more sterically restrictive bridge groups between the reactive moieties cure more slowly, yet also more completely. The favorable physical properties of these resins suggest that they are appropriate for demanding environments with a variety of potential uses in military and commercial applications.

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STRUCTURE/PROPERTY RELATIONSHIPS OF CYANATE ESTER RESINS FROM RENEWABLE SOURCES

11 April 2013

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Outline

- Background / Motivation
  - About Cyanate Esters
  - Why Study Non-Petroleum Feedstocks for Cyanate Esters?
- Properties of Creosol-Based Cyanate Esters
  - Effect of Bridging Group
  - Comparison to Common Dicyanate Esters
- Program Integration / Future Work

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More details in: Meyelmans et al., *Biomacromolecules*, 2013:
doi: 10.1021/bm3018438

AFRL Mission

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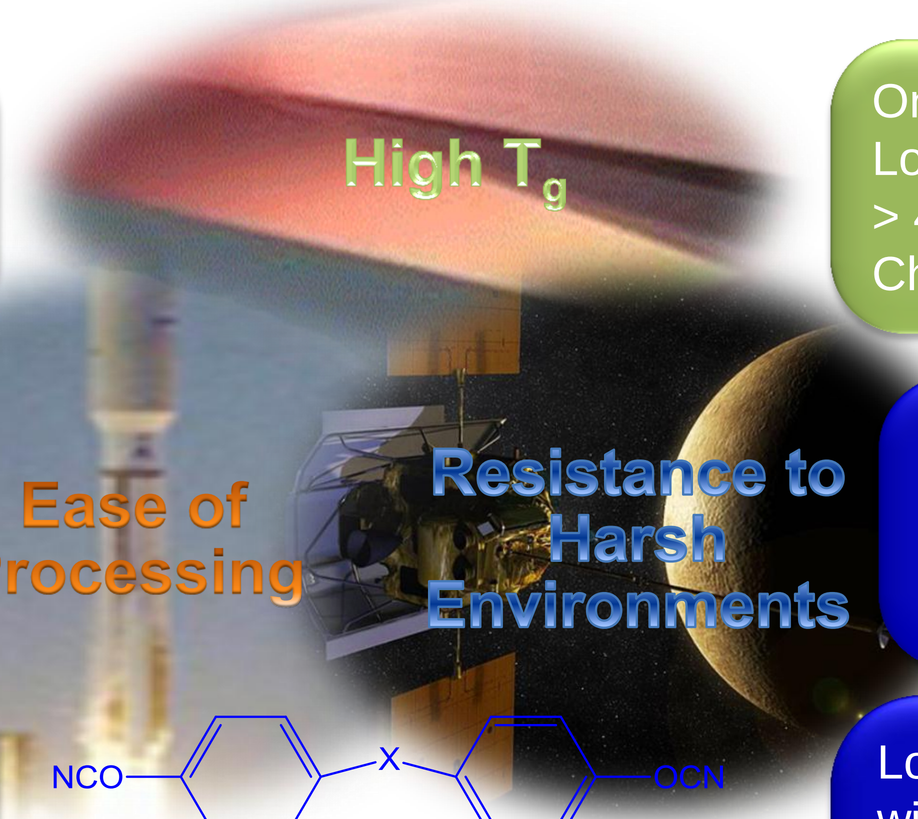
Cyanate Esters for Next-Generation Aerospace Systems

Glass Transition Temperature
200 – 400 °C (dry)
150 – 300 °C (wet)

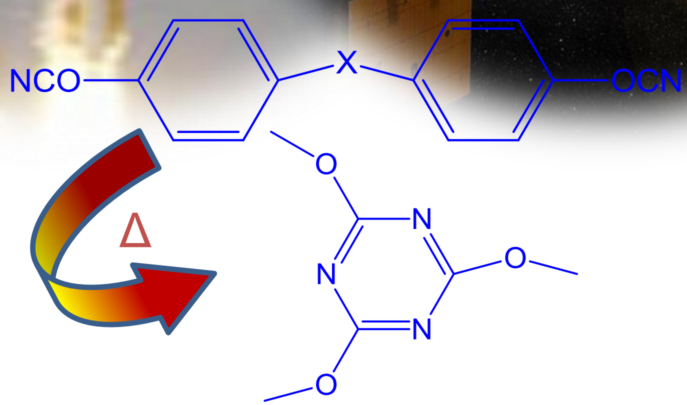
Onset of Weight Loss:
> 400 °C with High Char Yield



Resin Viscosity Suitable for Filament Winding / RTM

Good Flame, Smoke, & Toxicity Characteristics

Compatible with Thermoplastic Tougheners and Nanoscale Reinforcements

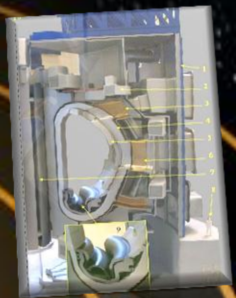


Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion

Cyanate Esters Around the Solar System

Our Solar System

- On Earth, cyanate ester / epoxy blends have been qualified for use in the toroidal field magnet casings for the ITER thermonuclear fusion reactor



Fusion reactor, photo courtesy of Gerritse ((Wikimedia Commons)

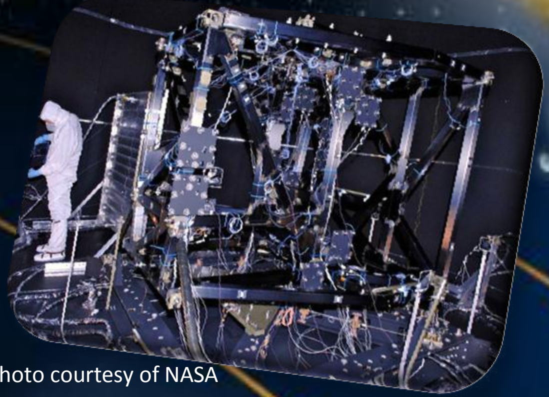
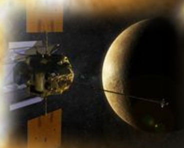


Photo courtesy of NASA

- Unique cyanate ester composites have been designed by NASA for use as instrument holding structures aboard the James Webb Space Telescope

- The science decks on the Mars Phoenix lander are made from M55J/cyanate ester composites



- The solar panel supports on the MESSENGER space probe use cyanate ester composite tie layers

Images: courtesy NASA (public release)

Why Bio-Based Cyanate Esters

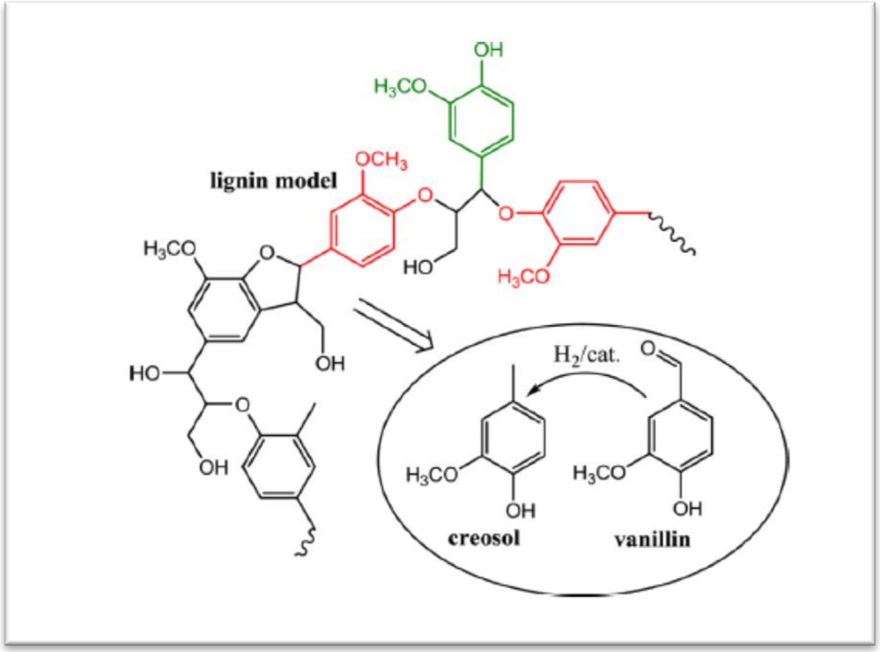
- Materials qualification efforts are costly; developing bio-based materials that deliver both improved performance and decreased dependence on petroleum enables a higher and more robust return on investment
- Cyanate esters are generally easy to process; they do not require stoichiometric balance and form co-networks readily, hence they tolerate variation in monomer chemistry relatively well


U.S. Navy photo by Photographer's Mate 3rd Class Mark J. Rebilas (RELEASED)

- The superior flame, smoke, and toxicity characteristics of cyanate esters, the excellent adhesion and durability characteristics of the networks, and the very high selectivity of the reaction (which makes de-polymerization easier), all confer benefits from a sustainability perspective
- Bio-based feedstocks for cyanate esters are interesting because of the combinations of physical properties provided by structure of the molecules themselves, not just because of the cost or environmental impacts

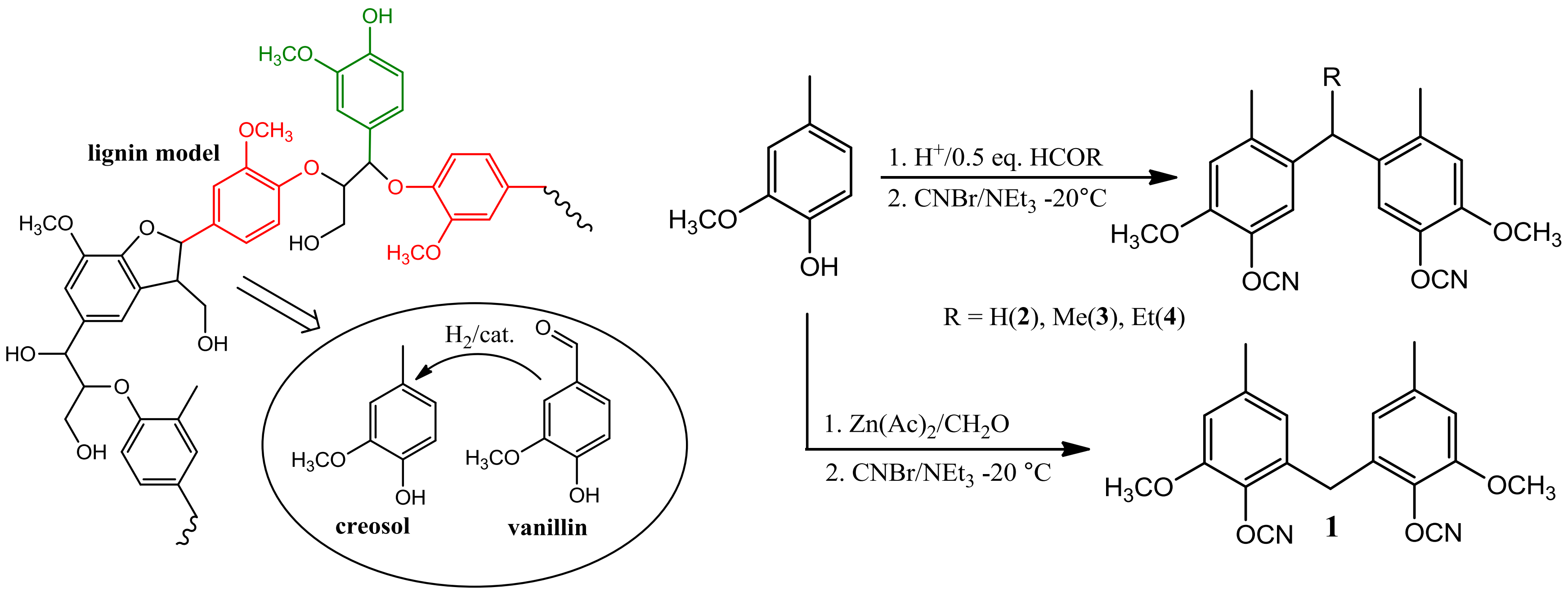
Creosol as a Monomer Source

Image source: Wikimedia Commons (user chmee2)



- Input material cost is an important consideration for cyanate ester resins
- Lignin is available in large quantities (DoE estimates ~200MT/yr by 2030) from sources such as wood
- The large available quantities, as well as suitability of co-production with cellulose for fuel, make for a low potential feedstock price

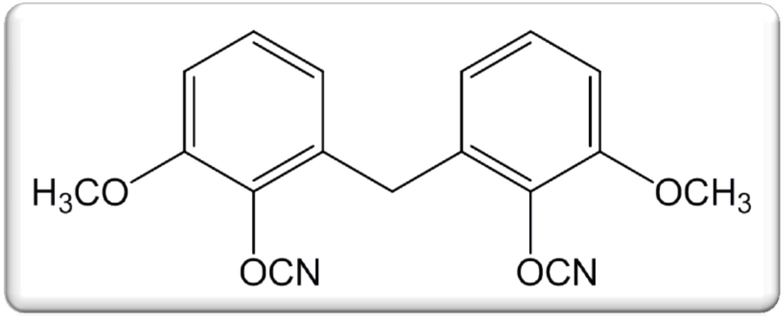
Overview of Creosol-Based Monomer Synthesis



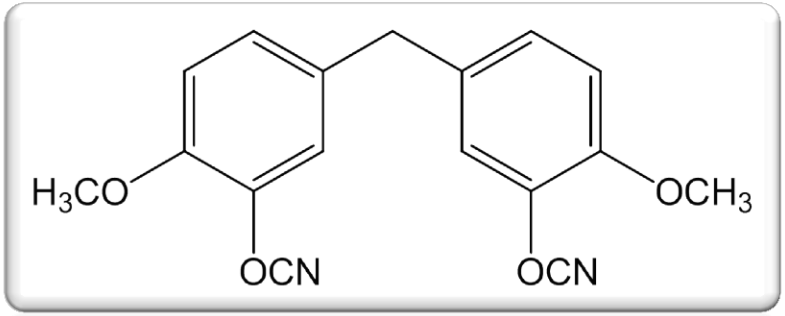
- Creosol and vanillin can be extracted from lignin
- Oxidative and reductive coupling reactions lead to precursor phenols, which are then treated with cyanogen bromide to generate cyanate ester monomers
- As in traditional synthesis of bisphenol products, the aldehyde used for coupling may be varied to produce a variety of bridge groups

Creosol-Based Cyanate Esters: Variety of Bridging Groups

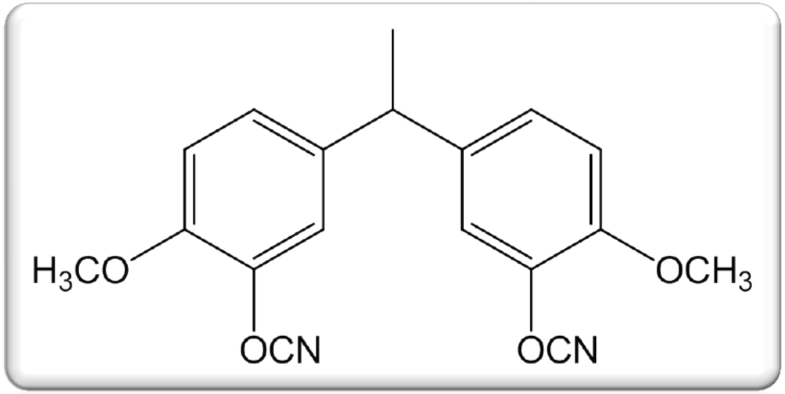
CE-C1



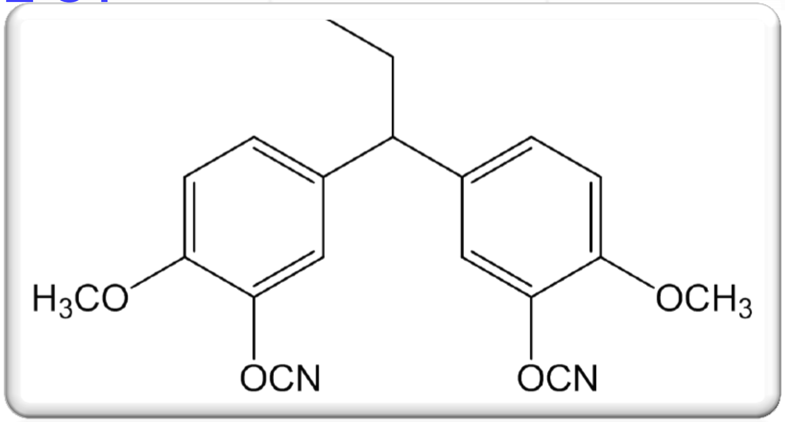
CE-C2



CE-C3



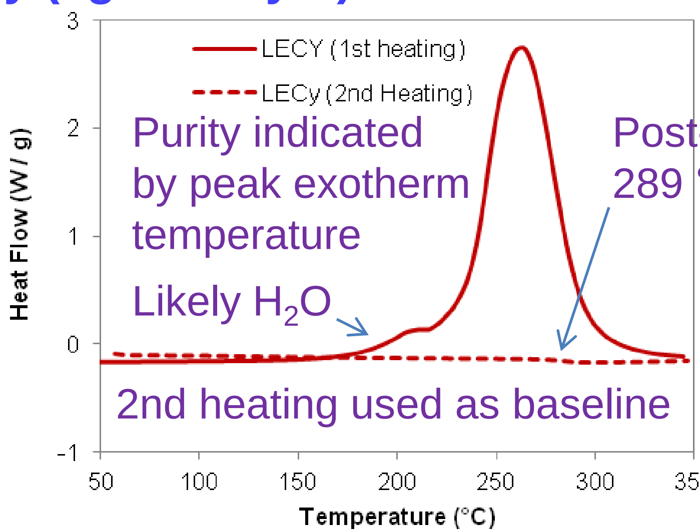
CE-C4



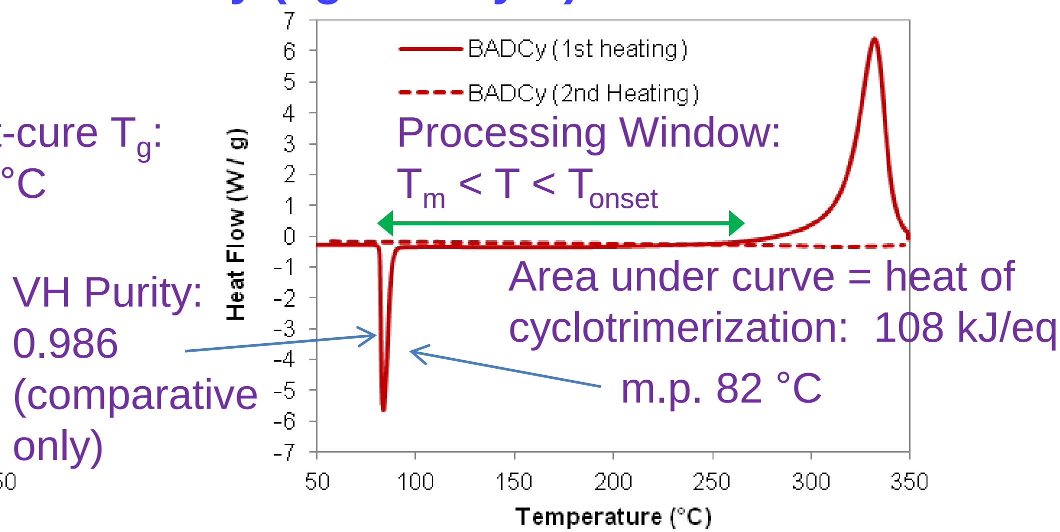
- Note the difference in linkage between C1 (more hindered) and C2 (less hindered but dissimilar to 4,4’ linkage in commercial dicyanate esters)
- CE-C3 is analogous to commercial Primaset® LECy with methoxy groups added and 3,3’ linkage

Assessment of Processing Characteristics via DSC

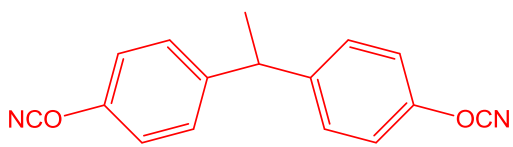
LECy (aged 3.5 yrs)



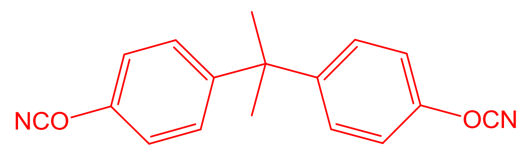
BADCy (aged 2.5 yrs)



LECy



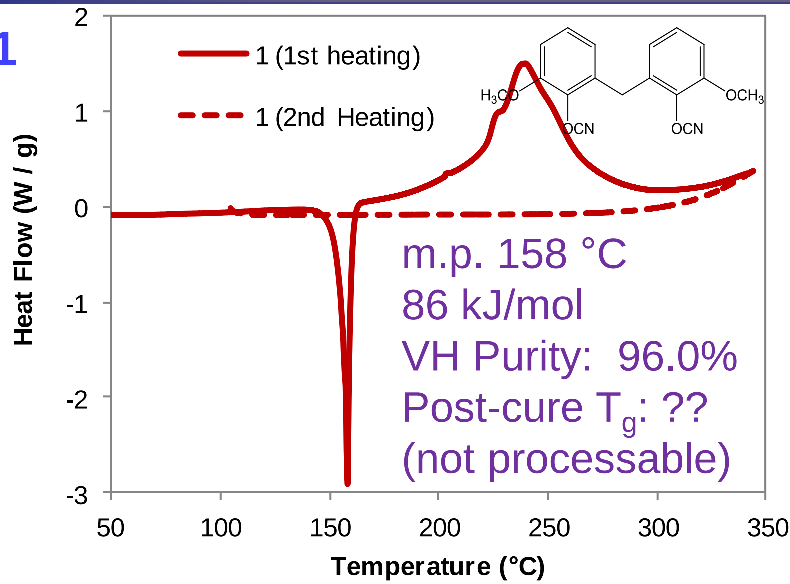
BADCy



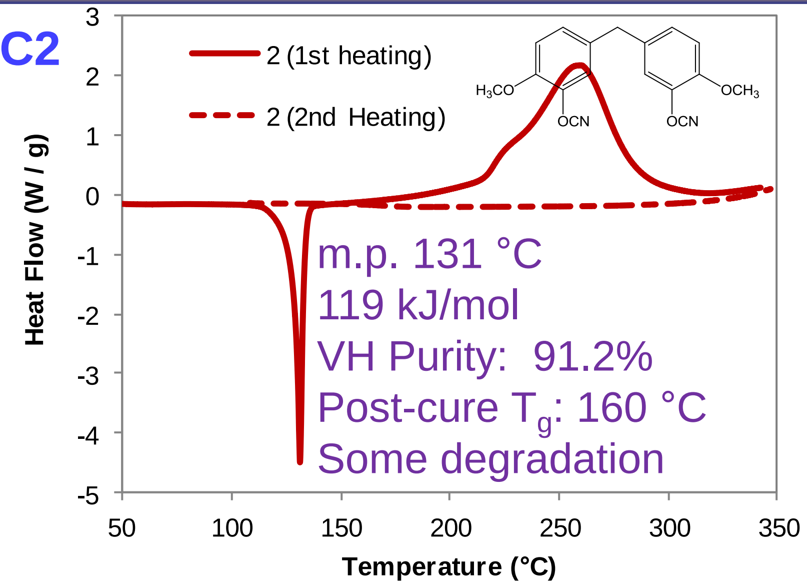
- Cyanate esters typically show an exotherm of about 110 kJ/eq.; lower values tend to indicate incomplete cure of –OCN groups
- The distance between the melting endotherm and the cure exotherm indicates the processing window for the material (wider, and at lower temperature, is better)

DSC of Creosol-Based Cyanate Esters

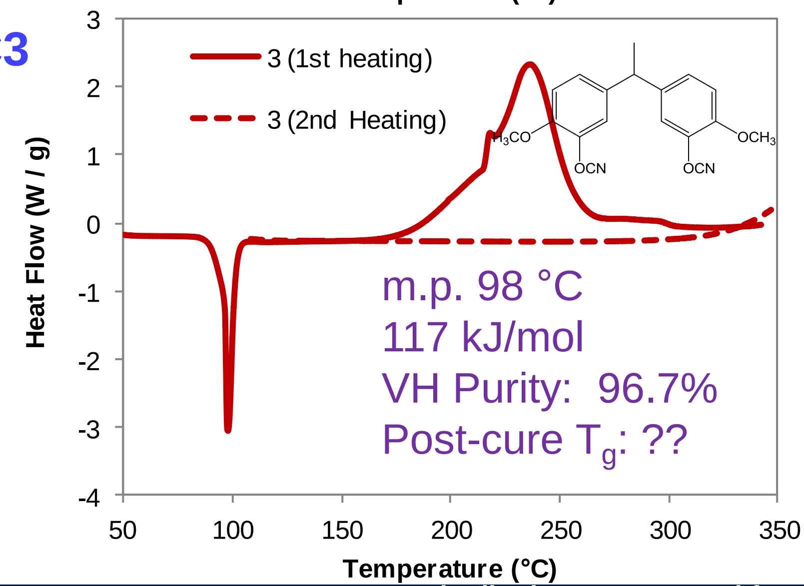
CE-C1



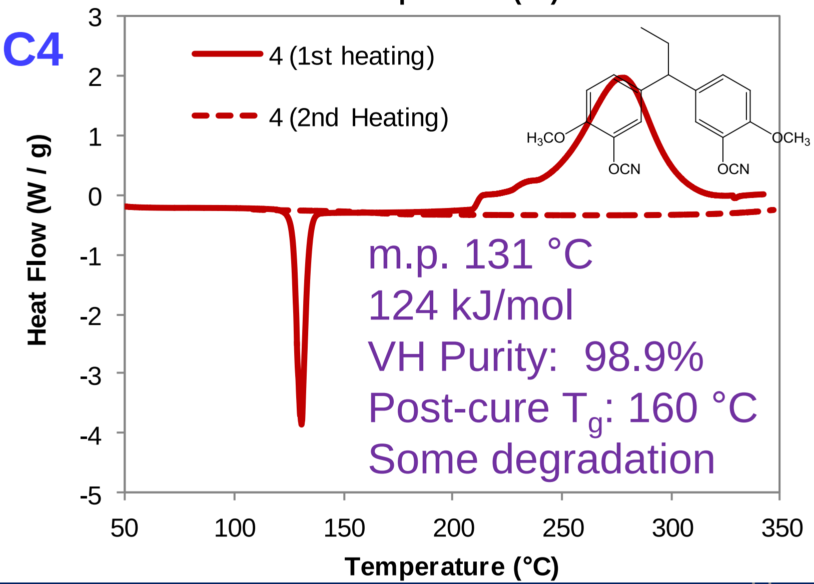
CE-C2



CE-C3

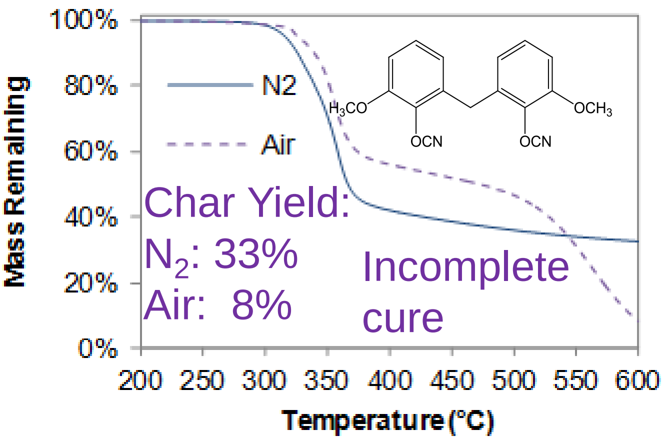


CE-C4

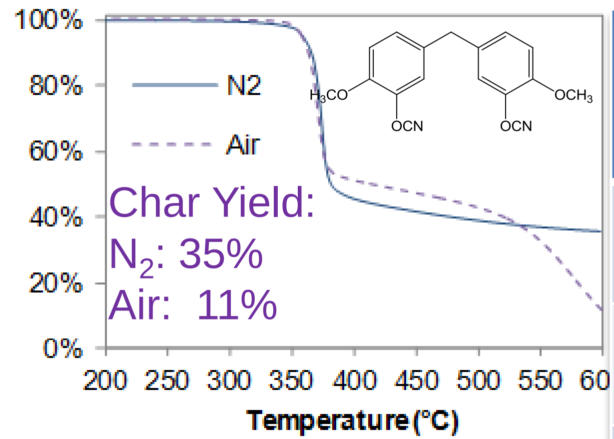


Thermochemical Stability of Creosol-Based Cyanate Esters

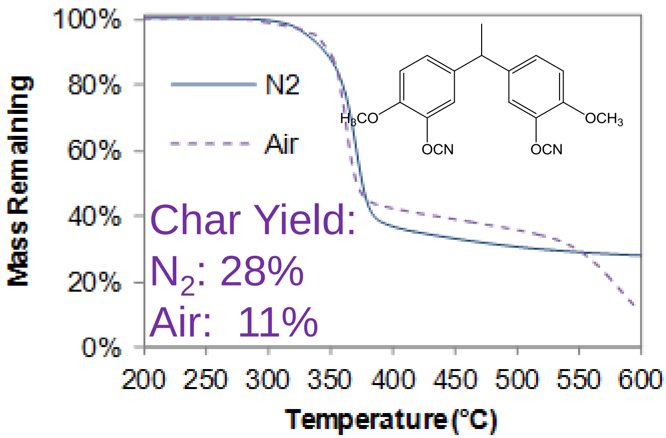
CE-C1



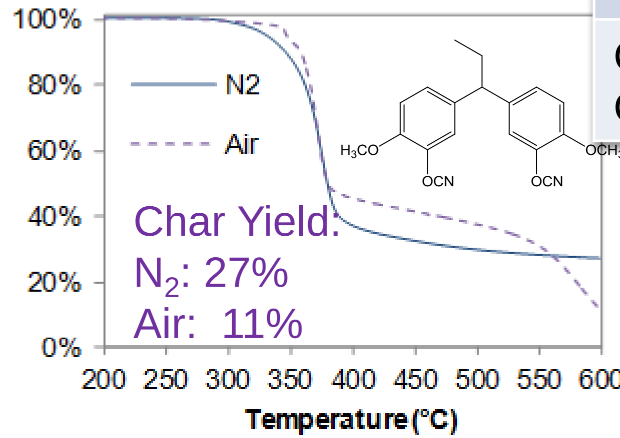
CE-C2



CE-C3



CE-C4



Network Composition:

	Wt % Aro-matic	Wt % Aliph-atic	Wt % OCN
CE-C1	48	25	27
CE-C2	48	25	27
CE-C3	46	28	26
CE-C4	44	31	25

Comparisons with commercial cyanate esters indicate the methoxy groups play a significant role in decomposition

Physical Properties of Creosol-Based Cyanate Esters

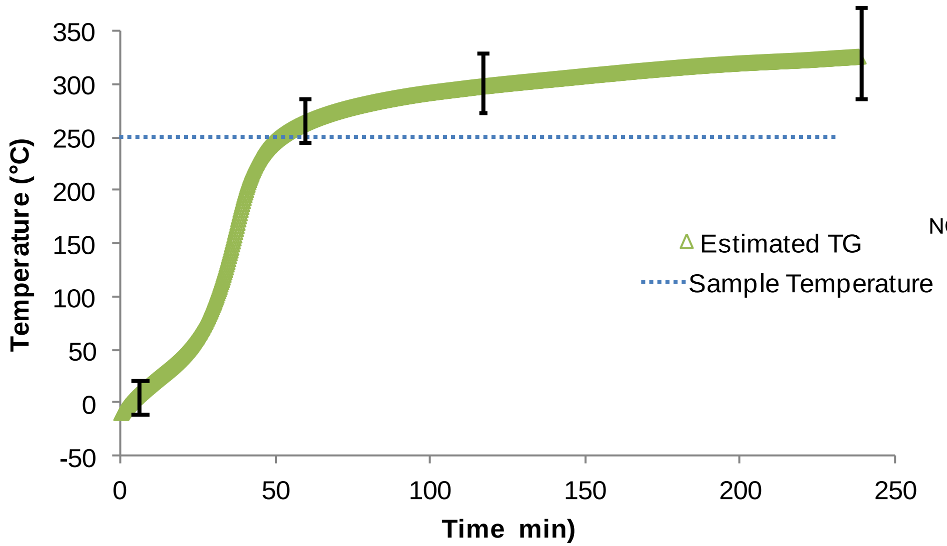
Com-pound	Density (g/cc)	Cyanurate Density at Full Cure (mmol/cc)	As-Cured Dry T_g by TMA (°C)	T_g After Post-Cure to 350 °C in TMA (°C)	"Wet" T_g After 96 h Immersion in 85 °C H_20 (°C)	Water Uptake
CE-C1	1.237	2.59	172	166	165	2.05%
CE-C2	1.223	2.56	255	243	184	2.05%
CE-C3	1.198	2.41	253	196	178	2.61%
CE-C4	1.190	2.29	254	198	161	3.21%

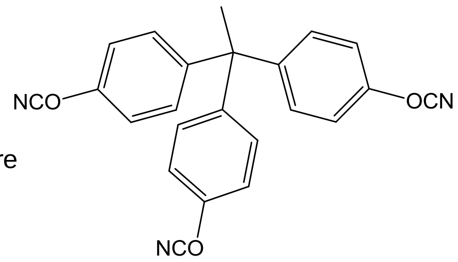
- CE-C1 and CE-C2 are isomers; the higher density of CE-C1 is likely due to incomplete cure
- CE-C1 showed excessive creep in "as-cured" samples; samples post-cured to 250 ºC in the TMA showed a loss peak at 235 ºC and only moderate creep
- Samples CE-C3 and CE-C4 suffered severe damage on heating past 300 ºC due to volatiles, which is reflected in their lower post-cure T_g (may take place to lesser extent in CE-C2).
- Water uptake generally higher than comparable commercial dicyanate products; methoxy substitution may increase water uptake

Samples CE-5 through CE-7 cured at 150 ºC for 1hr then 210 ºC for 24 hrs under dry nitrogen. Initial cure temperature for sample CE-4 was 170 ºC due to its high melting point.

The Similarity of “As Cured” Glass Transition Temperatures

Typical Example of T_g Development in Uncatalyzed Cyanate Ester During Cure





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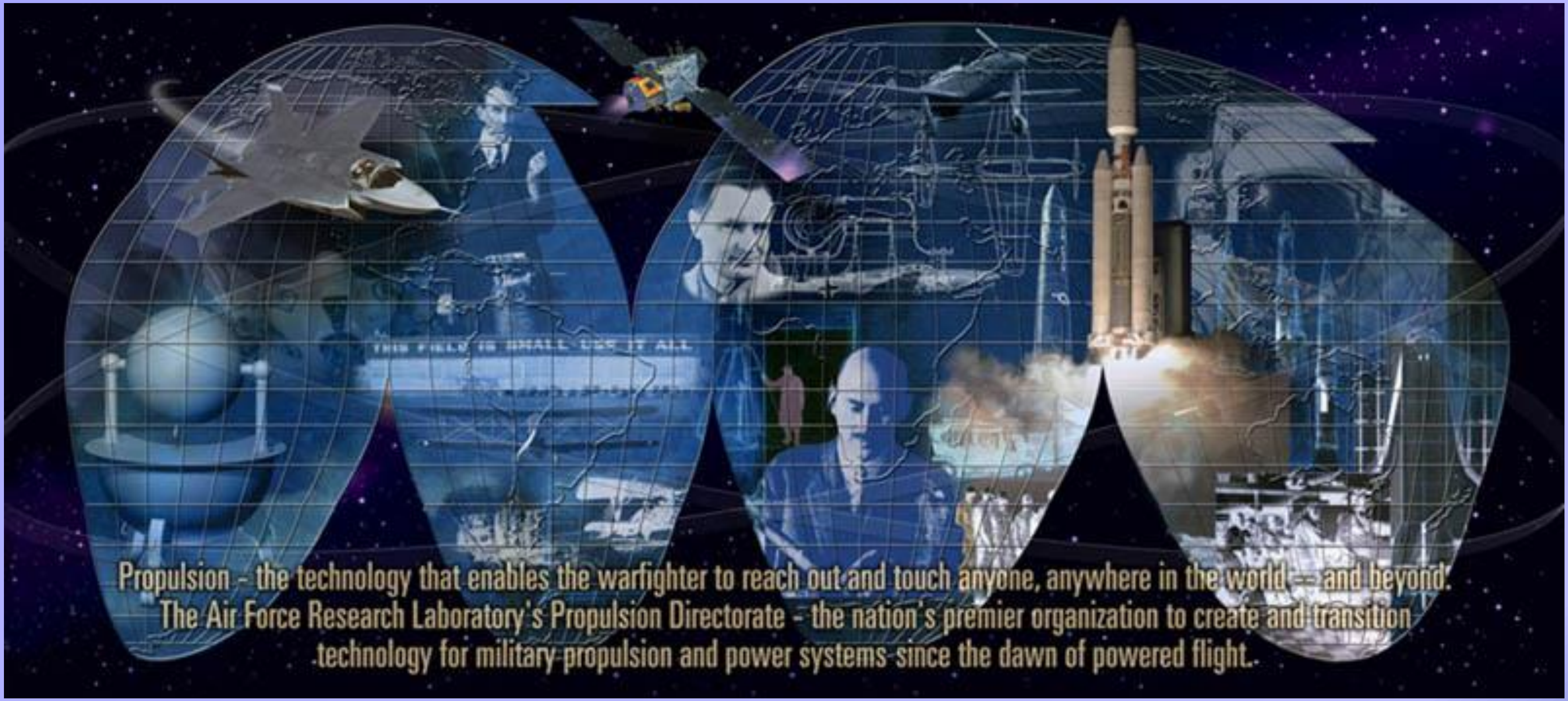
- When the glass transition temperature exceeds the cure temperature (as almost always happens in cyanate ester cure), the rate of cure slows down rapidly.
- The point at which cure decelerates significantly is primarily determined by cure temperature, not chemical structure
- For long cure periods, differences in cure kinetics affect only the initial part of the glass transition temperature development curve
- These effects combine to produce a very similar glass transition temperature for many different cyanate esters when cured for long periods in the glassy state

Summary / Future Work

- Creosol can be converted to a wide variety of dicyanate monomers via multiple forms of coupling chemistry
  - The configurational chemistry of the coupling point relative to the cyanate ester groups is critical for processability (2,2’ coupling produces incomplete cure, whereas 3,3’ (demonstrated here) and 4,4’ (commercial) produce complete cure with a viable processing window
  - When complete cure takes place, the resin achieve “process limited” glass transition temperature values at or above 250 °C
  - The presence of methoxy groups leads to decreased thermal stability compared to commercial dicyanate ester monomers, however, good thermo-chemical performance, with degradation onset temperatures well above 300 °C, is maintained

- Areas for future work
  - Glass transition temperatures at full cure needed to assess impact of bridge structure on extent of cure and range of available physical properties
  - Mechanisms of thermo-chemical degradation and impact on water uptake of methoxy functionality needs to be better understood



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